

Magnetization and magnetostriction of Van Vleck
antiferromagnets with magnetic anisotropy of
"easy-plane" type

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1 февраля 2008 г.

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The theoretical description of quantum phase transition, induced by the external magnetic field, into antiferromagnetic state in the Van Vleck – singlet – magnet with single-ion anisotropy of "easy-plane" type and ion spin $S = 1$ is proposed. It is shown that the spin polarization of the ground non-degenerated state proves to be the order parameter of such a transition and that the Landau thermodynamic approach can be employed for its (transition) description. The magnetic properties which include the field behavior of magnetization and magnetic susceptibility of the antiferromagnetic phase in the fields of different directions are studied. The peculiarities of induced magnetostriction in Van Vleck antiferromagnet, which as well as magnetization has a singularity in the phase transition point, are investigated. An attempt is made for qualitative comparison of results obtained with available experimental data.

PACS number(s): 75.10.-b, 75.10.Jm, 75.30.Gw, 75.30.Kz, 75.50.Ee

1 Introduction

It is well known, that magnetization of the classical (or, what is the same, weakly anisotropic) antiferromagnet at low temperatures (far below Neel one T_N), is connected with sublattice magnetizations turn only [1]. From this fact, it is usually supposed that their magnitude remains constant, and under the effect of the external magnetic field only their directions are changing. The character and peculiarities of magnetization process (spin-flip, spin-flop and also orientation phase transitions of the 1st kind) in such antiferromagnets depend on the next parameters: value and direction of the external magnetic field, anisotropy constants, and the magnitude of intersublattice exchange [2-5]. For example, in "easy-plane" two-sublattice dihalogenids NiCl_2 or CoCl_2 of iron group field behavior of magnetization [6-10] is well satisfied by quasi-classical approach, although these magnets defer significantly. The value of "easy-plane" single-ion anisotropy in NiCl_2 is much less than exchange – each ion orbital moment in crystal field is practically fully frozen. At the same time there is only partial freezing of orbital moment in CoCl_2 , and the "easy-plane" single-ion anisotropy is approximately the half of exchange (by order of its value [7]). The field behavior of induced magnetostriction of these crystals [11-13] are also agreed with idea of rotation of preserving by module of sublattice magnetizations.

Among antiferromagnets there are, however, some family of crystals, in which single-ion anisotropy exceeds inter-ion exchange [14,15] – it is so-called Van Vleck, or singlet, antiferromagnets. The magnetic ordering in them is absent at all temperatures, up to

$T = 0$. Such materials include, in particular, hexagonal crystals of ABX_3 type, where A is the ion of alkali metal ($A = \text{Cs, Rb}$), B is the transition metal ($B = \text{Fe}$), X is the halogenide ($X = \text{Cl, Br}$). In these crystals magnetic moments, induced by external field on paramagnetic ions B^{2+} , form antiferromagnetic chains along C_3 axis, on the one hand, and, on the other, – triangular structures in basic plane (see reviews [16-19]). There are also some other compounds, that refer to Van-Vleck antiferromagnets, and among them so-called DTN, which chemical formula is $\text{NiCl}_2 \cdot 4\text{SC}(\text{NH}_2)_2$ [20-23]. It also has (antiferromagnetic) chains Ni-Cl-Cl-Ni along "heavy" magnetic axis, although in field absence the mean spin on each site is equal to zero, because of exceeding by single-ion anisotropy of parameters of both intra- and intersublattice exchange. It should be emphasized, that DTN can be referred to the group of two-sublattice Van Vleck antiferromagnets, that have different from NiCl_2 crystal structure, another character of exchange interactions, which by the value are much less than single-ion anisotropy [22,23].

The magnetization process in Van Vleck antiferromagnets differs principally from that which takes place in classical Neel antiferromagnets [25-28]. At first, the magnetic ordering without external magnetic field is absent and therefore there are no any magnetic sublattices. Secondly, magnetic, or particularly antiferromagnetic, ordering in Van Vleck antiferromagnets can appear spontaneously by quantum (in definition of Ref. [24]) phase transition, induced by magnetic field [16-23].

Weak dependence of magnetic susceptibility on external magnetic field, thus, represents some sort of peculiarity of antiferromagnetic phase. As a result, the observed magnetization actually follows the linear field behavior [22,23,29,30]. It appears, in other words, that such a behavior of magnetization of a system (but not the proper sublattice magnetization) in antiferromagnetic phase is similar to the magnetization induced by external field in Neel antiferromagnets. It could be understood, if the transition to the antiferromagnetic phase would be the phase transition of the 1st kind. In such a case sublattices could magnetize, in the transition point, due to jump (in the presence of corresponding susceptibility singularity), and at further field growth there can occur sublattice magnetic vectors turn only. The experiment shows, however, that transformation of non-magnetic (singlet) state in the antiferromagnetic one takes place continuously, what means, that this magnetic transformation is the phase transition of 2nd kind [22,23,29,30]. The latter demonstrates, that sublattice magnetizations appear and change also continuously from their initial zero value to maximal one. So, the classical approach with the constant module of sublattice average spin for Van

Vleck antiferromagnets is not applicable fundamentally.

The results of DTN induced magnetostriction measurements are presented in the papers [22,23]. It could be seen from them, particularly, that induced magnetostriction in DTN appears and exists namely in the antiferromagnetic phase only. There was also found, that relative crystal deformation, that arises along "heavy" magnetic axis, changes its sign during field increasing. Such a behavior of DTN striction was attributed in Ref. [23] to the prevailing role in this compound of intersublattice magnetoelastic interaction of exchange nature [20,21]. On the other hand, the magnetostriction sign change is also observed in some classical Neel antiferromagnets, for example in CoCl_2 [11-13], where it is conditioned by the anisotropic intrasublattice magnetoelastic interaction.

Thus, the description of induced magnetostriction in the Van Vleck antiferromagnets, where anisotropy is not small, and so, anisotropic magnetoelastic interaction also can be comparable (or even larger) with isotropic exchange one, becomes relevant. The consideration of this problem requires to account the fact, that sublattice magnetization modules in antiferromagnetic phase of the initially singlet magnet essentially depend upon the field.

From the above said it can be evident, that there are some unresolved questions of the description of induced magnetic phase transition into the antiferromagnetic phase and its magnetic characteristics (field dependencies of sublattice and system as a whole magnetizations, magnetic susceptibility, magnetostriction) in Van Vleck systems.

Below we shall proceed from the suggestion, that in Van Vleck magnets the intrinsic spontaneous magnetic (or antiferromagnetic) moment is equal to zero, so for them there is no magnetic ordering temperature without the external magnetic field. It would seem, that the absence of magnetic (dipole) moment, or, in other words, magnetization (spin) on the site, shows not only the absence of any magnetic ordering, but, clearly, the absence of the magnetic contributions in physical properties of corresponding systems. However, in fact, this is not right, because the absence of ordinary – exchange-induced – spin ordering do not include the presence the ordering of other type in, particularly, the quadrupole one. The latter, in one or other way, is peculiar to all Van Vleck magnets, which are the special case of magnetic crystals with more specific – nematic – type of spin ordering [31,32].

The one or another spin ordering proves itself not only by the appearance in crystal of new (spin-)electron excitation branches, which, for example, in Van Vleck nematics turn out gapped. It can also be revealed in such an observed and calculated characteristic of these magnets as their magnetostriction, which peculiarities for such systems is not completely

studied yet. At the same time, because of recent calculations of DTN magnetoelastic features [22,23], there is definitely such a need.

It can also be noted, that in some papers (for example, Refs. [33-36]), the description of phase transition between singlet and induced antiferromagnetic states carries out by using the representation of Bose-Einstein condensation of magnons. Indeed, the appearance of magnetization in finite magnetic fields can be formally described in the terms of some magnetic excitations condensation. But in reality in observed systems there does not occur any true condensation of quasiparticles, because, as it will further be seen, one should say about rearrangement of the ground state only, and thus – about virtual, but not real magnons [37].

Below there is considered the model of strongly anisotropic, two-sublattice antiferromagnet with ion bare spin $S = 1$. In the framework of quantum approach it will be made an attempt to describe the crystal magnetization, magnetic susceptibility and magnetostriction at magnetically induced phase transition from the initial singlet state to the spin-ordered one. For calculation of physical characteristics of a system, there will be used the total energy E , that is the sum of relevant contributions:

$$E = E_{exch} + E_{an} + E_h + E_{el} + E_{m-el}, \quad (1)$$

where E_{exch} is the exchange energy; E_{an} is the magnetic anisotropy energy; E_h is Zeeman energy; E_{el} is the elastic energy and E_{m-el} is the magnetoelastic energy, or the energy of spin-lattice coupling. It is also supposed, that magnetoelastic interactions are much weaker than exchange ones, and do not have a noticeable feed-back influence on the magnetic ordering. Assumptions made allow to provide a calculation in the simplest, but rather general form, confining, as usual, by summands, that are linear by elastic deformation tensor in the magnetoelastic energy and are quadratic by this tensor in elastic energy. So, at this limitations, there can be solved a problem of the magnetic ordering, at first, and only then use obtained results for field dependence of induced striction.

2 The ground state of singlet antiferromagnet with $S = 1$ and "easy-plane" magnetic anisotropy in the longitudinal magnetic field

In accordance with above mentioned the consideration will be for simplicity restricted by bilinear anisotropic (intra- and intersublattice) exchange interactions, single-ion "easy-plane" anisotropy and Zeeman term. The simplest model Hamiltonian of a system, that defines three contributions, E_{exch} , E_{an} and E_h , in Eq. (1), can be written as:

$$H = \frac{1}{2} \sum_{\mathbf{n}_\alpha, \mathbf{m}_\beta} J_{\mathbf{n}_\alpha \mathbf{m}_\beta} \mathbf{S}_{\mathbf{n}_\alpha} \mathbf{S}_{\mathbf{m}_\beta} + \frac{1}{2} \sum_{\mathbf{n}_\alpha, \mathbf{m}_\beta} J_{\mathbf{n}_\alpha \mathbf{m}_\beta}^Z S_{\mathbf{n}_\alpha}^Z S_{\mathbf{m}_\beta}^Z + D \sum_{\mathbf{n}_\alpha} (S_{\mathbf{n}_\alpha}^Z)^2 - h_{\parallel} \sum_{\mathbf{n}_\alpha} S_{\mathbf{n}_\alpha}^Z, \quad (2)$$

where $\alpha, \beta = 1, 2$ are the magnetic sublattice indices, which numbers in the considered system was chosen as 2; vectors \mathbf{n} and \mathbf{m} gives spins position in magnetic sublattices, which are described by spin operators $\mathbf{S}_{\mathbf{n}_\alpha}$; the constant $D > 0$, that reflects an "easy-plane" magnetic structure; the magnetic field h is defined in units of energy, so $h_{\parallel} = \mu_B g H_Z$; H_Z is the OZ projection of magnetic field, at that the crystallographic symmetry axis OZ is perpendicular to the "easy" plane. Just at the $\mathbf{h} \parallel OZ$ the magnetic field induce the phase transition to the antiferromagnetic state. The case of transverse field $\mathbf{h} \perp OZ$ will also be considered below, but it should be emphasized, that such a field do not induce any phase transitions. Parameters $J_{\mathbf{n}_\alpha \mathbf{m}_\beta}$ characterize the value of exchange interaction isotropic part and $J_{\mathbf{n}_\alpha \mathbf{m}_\beta}^Z$ is exchange anisotropy, which can be basically both "easy-axis" and "easy-plane" types. We, however, will assume, that inter-ion anisotropy, as also single-ion one, relates to the same – "easy-plane" – type.

The convenience of these restrictions is conditioned by the fact, that in such a physical situation both sublattices become symmetric relatively to the external field, what allows to reduce twice the number of equation derived.

The analysis of possible quantum eigenstates of Hamiltonian (2) at $\mathbf{h} \parallel OZ$ will be provided, using the approximation of self-consistent field, that corresponds to spin fluctuation neglecting and to the change of average by multiplying spin operators of different sites on multiplying of averages. In this case the energy E_{gr} of the ground state, normalizing on one cell (for nearest both inter- and intrasublattice different spins) is equal to:

$$E_{gr} = \frac{1}{2} \sum_{\alpha\beta} J_{\alpha\beta} z_{\alpha\beta} \mathbf{s}_\alpha \mathbf{s}_\beta + \frac{1}{2} \sum_{\alpha\beta} J_{\alpha\beta} z_{\alpha\beta} s_\alpha^Z s_\beta^Z + D \sum_{\alpha} Q_\alpha^{ZZ} - h_{\parallel} \sum_{\alpha} s_\alpha^Z \quad (3)$$

where \mathbf{s}_α is the quantum-mechanical average of spin vector of α th sublattice in the ground ion state; $z_{\alpha\beta}$ is the number of nearest neighbors from the same ($z_{\alpha\alpha}$) and another ($z_{\alpha\beta} \equiv z_{12}$) sublattices. Also here are introduced such averages for components of spin quadrupole moment Q_α^{ZZ} [40-42]. It should be also noted that for antiferromagnet the intersublattice exchange parameter is $J_{12}z_{12} \equiv I > 0$; at the same time, the parameter $J_{11}z_{11} = J_{22}z_{22} \equiv J$ of intrasublattice exchange can be of any sign, that we will also choose for simplicity as furthering to the ordering, $J < 0$. The exchange anisotropy, in this case, satisfies the conditions of its "easy-plane" type: $J_{12}^Z z_{12} \equiv \Delta I < 0$ and $J_{11}^Z z_{11} = J_{22}^Z z_{22} \equiv \Delta J > 0$.

Let us impose for spins of each sublattice their proper (rotating) coordinate systems $\xi_\alpha \eta_\alpha \zeta_\alpha$, that α th sublattice average spin is always oriented along ζ_α axis, what means that this axis is the quantization one for this spin sublattice, and ξ_α axis is lain in $Z\zeta_\alpha$ plane. Thus, in such coordinate systems the correct wave function of the α th sublattice ground spin state, as well known, has next form [38,39]:

$$\psi_\alpha^{(0)} = \cos \phi_\alpha |1\rangle + \sin \phi_\alpha |-1\rangle, \quad (4)$$

where $|\pm 1\rangle$ and $|0\rangle$ are eigenfunctions of operator $S_{\mathbf{n}_\alpha}^\zeta$ in bra-ket representation. Next, it can be calculated, using (4) the quantum-mechanical spin and quadrupole averages:

$$s = \cos 2\phi, \quad Q^{\zeta\zeta} = 1, \quad Q^{\xi\xi} = \frac{1}{2} (1 + \sin 2\phi). \quad (5)$$

In the expressions (5) the sublattice indices are missed, because as mentioned at the chosen field direction the evident dependence of observables on index α is absent.

The usage of functions (4) allows one to describe the energy (3) at $\mathbf{h} \parallel OZ$ as:

$$E_{gr} = I \cos^2 2\phi \cos 2\theta - |J| \cos^2 2\phi - J_Z \cos^2 2\phi \cos^2 \theta + 2D \left[\cos^2 \theta + \frac{\sin^2 \theta}{2} (1 + \sin 2\phi) \right] - 2h_{\parallel} \cos \theta \cos 2\phi, \quad (6)$$

where $J_Z \equiv \Delta J - \Delta I$.

For the determination of magnetization, magnetic susceptibility and subsequently striction, there should be found field behavior of mean spin (and its direction) for each sublattice in

the field. Also it should be made the same calculation for spin quadrupole moment. As it was reported in Refs. [40,41], the solution of the problem of spin configuration in the magnetic field consists of the minimization of the expression (6) by all available unknown quantities: the geometrical angle θ and (see Eq. (4)) the angle ϕ of quantum states mixture. Such a method of observables finding, being completely an equivalent to the solution of quantum self-consistent problem, is more convenient and consistent, because allows the generalization on the case of finite temperatures [27,28].

The equations for both required angles are:

$$\frac{\partial E_{gr}}{\partial \phi} = -2(I \cos 2\theta - |J| + J_Z \cos^2 \theta) \sin 4\phi + 2D \sin^2 \theta \cos 2\phi + 4h_{\parallel} \cos \theta \sin 2\phi = 0, \quad (7)$$

$$\frac{\partial E_{gr}}{\partial \theta} = -(2I + J_Z) \sin 2\theta \cos^2 2\phi - D \sin 2\theta (1 - \sin 2\phi) + 2h_{\parallel} \sin \theta \cos 2\phi = 0. \quad (8)$$

It is known from Ref. [37], that the set of Eqs. (7)-(8) in the absence of the external magnetic field has two solutions: the non-magnetic one, $s = 0$, that exists at $D > 2(I + |J|)$ and the "magnetic" one at $D \leq 2(I + |J|)$, with which the reduced value of single-site mean spin

$$s = \sqrt{1 - \frac{D^2}{4(I + |J|)^2}} < 1 \quad (9)$$

is associated.

The initial ground state of the system should be the singlet one, $s = 0$, that the quantum phase transition (at the magnetic field $\mathbf{h} \parallel OZ$) from this state to magnetically ordered one occurs. So, below we will suppose, that the next evident inequality $2(I + |J|)/D < 1$ takes place. At this model parameters ratio, the ground state of the system is really nonmagnetic and the ordering in the absence of magnetic field is not realized at any temperatures [41]. Otherwise, this ratio actually gives the condition on singletness of magnet ground state, which is Van Vleck one. The solution $s = 0$ also satisfies Eqs. (7)-(8) for some interval of magnetic fields.

As field grows the finite value, $s \neq 0$, of the mean spin on the site appears. It can be derived from Eq. (8) the expression for the average spin orientation relatively to the crystallographic axis:

$$\cos \theta = \frac{h_{\parallel} \cos 2\phi}{D(1 - \sin 2\phi) + (2I + J_Z) \cos^2 2\phi}. \quad (10)$$

It is seen from Eqs. (7) and (10), that in large fields, when $h_{\parallel} \geq h_{flip}$ (where $h_{flip} \equiv D + 2I + J_Z$) the state, in which spins of both sublattices are directed along "heavy" ($\theta = 0$)

axis, is established. Then the spin projection on the external field direction will be maximum and equal to $s = S = 1$. For $h_{\parallel} < h_{flip}$ spins of sublattices are orientated at finite angle $0 < \theta \leq \pi/2$ to the "heavy" axis.

3 Thermodynamic analysis of spin states

Using the formulas (5) and substituting Eq. (10) into the Eq. (6), it could be obtained the ground state energy in the form of functional

$$E_{gr} = -(I + |J|) s^2 + D \left(1 - \sqrt{1 - s^2} \right) - \frac{h^2 s^2}{D (1 + \sqrt{1 - s^2}) + (2I + J_Z) s^2}, \quad (11)$$

which depends on the spin polarization \mathbf{s} only. The expansion of this energy over the small s gives:

$$E_{gr} = \frac{h_s}{D} (h_s - h_{\parallel}) s^2 + \frac{D}{8} \left(1 + \frac{2h_s^2 (2I + J_Z)}{D^3} \right) s^4 \quad (12)$$

where $h_s = D\sqrt{1 - 2(I + |J|)/D}$ is the critical field of magnetization appearance.

In the expansion (12), which refers to the field region $h_{\parallel} \rightarrow h_s$, one can restrict by terms, that are not higher then of 4th power by s . Actually this expansion for the ground state energy is similar to the free energy expression in Landau theory of phase transitions. However, in Eq. (12) the ground state spin polarization corresponds to the order parameter, and the leading parameter, that results in the phase transition, is not the temperature, but the magnetic field. It can be seen from Eq. (12), that at $h_{\parallel} < h_s$ the coefficients at s^2 and s^4 are positive, and so the ground state of spin system will be Van Vleck non-magnetic single-ion state. At the pint $h_{\parallel} = h_s$ the sign of coefficient at s^2 changes, and in the fields $h_{\parallel} > h_s$ the spin polarization (of still non-degenerate ground state) spontaneously appears. The value of polarization can be readily found by minimization of E_{gr} (12):

$$\frac{\partial E_{gr}}{\partial s} = 2s \left[\frac{h_s}{D} (h_s - h_{\parallel}) + \frac{D}{4} \left(1 + \frac{2h_s^2 (2I + J_Z)}{D^3} \right) s^2 \right] = 0. \quad (13)$$

From Eq. (13) it follows, that near the critical point $h_{\parallel} \geq h_s$ this polarization (or simply the spin of the ground state) fundamentally depends on the field:

$$s(h_{\parallel}) = \sqrt{\frac{4h_s (h_{\parallel} - h_s)}{D^2 + 2h_s^2 (2I + J_Z) / D}}. \quad (14)$$

In the same vicinity, $h_{\parallel} \geq h_s$, of the critical point the angle θ between vector \mathbf{s} and axis OZ is determined by the expression:

$$\cos \theta = \frac{h_s}{2D} \sqrt{\frac{4h_s(h_{\parallel} - h_s)}{D^2 + 2h_s^2(2I + J_Z)/D}}. \quad (15)$$

Thus, it is found, at $h_{\parallel} = h_s$ the spin polarization spontaneously arises as field grows in the very "easy" plane, because at $h_{\parallel} - h_s \rightarrow 0$ the angle $\theta \rightarrow \pi/2$. In other words, it turns out, that in the moment of its appearance, the vector $\mathbf{s}(h_{\parallel} \geq h_s)$ is perpendicular to the longitudinal field: $\mathbf{s} \perp \mathbf{H} \parallel OZ$. Further magnetic field growth leads not only to the decreasing of θ , at it follows from Eqs. (14)-(15), but also to the simultaneous increasing of spin polarization, that is as bigger its value, as more it flatten against the "heavy" axis.

In the whole, the induced tilt of the magnetic sublattices, and thereafter the magnetization of Van Vleck antiferromagnet include two processes: the classical rotation of spins (sublattice magnetizations) and purely quantum (because of angle ϕ change) growth of single-site polarization $s(h_{\parallel})$. Both processes take place also at $T = 0$. The antiferromagnet magnetization (normalizing on one magnetic atom) is described by the evident product:

$$m_{\parallel} \equiv m(h_{\parallel}) = s(h_{\parallel}) \cos \theta = \frac{2h_s^2(h_{\parallel} - h_s)}{D^3 + 2h_s^2(2I + J_Z)} \quad (16)$$

As a result, one arrives to the unexpected result: the observed magnetization near critical field of quantum transition from singlet to spin-polarized state depends linearly – as in classical antiferromagnets – upon the external magnetic field, that induce the very transition. From this comes another rather remarkable conclusion: at such a phase transition the magnetic susceptibility of a system should have a jump.

Thus, in the framework of approach, that is similar to the Landau thermodynamic one, it was demonstrated, that the spin polarization is the only order parameter for induced by magnetic field $\mathbf{h} \parallel OZ$ quantum phase transition from Van Vleck phase to the antiferromagnetic one. But despite the fact, that calculation was made for the case $T = 0$, the required polarization proves to be essentially dependent on the external field. It should be reminded, that in classical antiferromagnets ion spin polarization is fixed at $T = 0$ and do not evaluate in the field, while in Van Vleck system it appears as a consequence (in terminology of Ref. [24]) of quantum phase transition [27,28].

Next an attention should be drowned to such an analogy, that single-ion anisotropy, reducing average spin, plays a role of "disordering" factor, and in this sense can be compared with entropy. It (single-ion anisotropy) leads to the mixture (or linear combination of quantum states), that results in the absence of spin polarization of ions in their ground state. The exchange and magnetic fields, on the contrary, resist to this, "magnetizing" the

system and causing the spontaneous (or forced) spin polarization, which at the moment of its appearance is directed perpendicularly to the magnetic field.

The studied quantum phase transition between Van Vleck (also ordered, in essential) and antiferromagnetic states is, as it was seen, the consequence of different interactions (exchange, Zeeman and spin-orbital, that lies at the heart of single-ion anisotropy) competition. Therefore such a quantum transformation is natural to identify as the magnetic phase transition of "displacement" but not of "order-disorder" type. As distinct from the last one, the transition of displacement type is not the transition in the system of spins, which fluctuate between degenerated (or almost degenerated) quantum states "up" and "down" because the ground state of quantum paramagnets is always non-degenerated and its polarization is the direct consequence of this state rearrangement in the external field.

There should be noted, at last, that the applicability of phenomenological theory, that is based on the expansion (11), is confined by the fields $h_{\parallel} \geq h_s$ in the vicinity of critical point h_s . In the field region $h_{\parallel} \gg h_s$ the magnetization process should be analyzed with more exact expressions both for ground state energy and for the equations, which define the spin configurations. However the latter can be easily found numerically.

4 The magnetization curves and magnetic susceptibility of antiferromagnetic phase

Substituting in the Eq. (11) the expression (5) the equation, that describes the spin polarization as the function of longitudinal field, can be obtained:

$$s \left(D - 2(I + |J|) \sqrt{1 - s^2} - \frac{D(1 + \sqrt{1 - s^2}) h_{\parallel}^2}{(D(1 + \sqrt{1 - s^2}) + (2I + J_Z))^2} \right) = 0. \quad (17)$$

It should be noted, that this equation refers both the fields $h_{\parallel} < h_s$ of the existence of Van Vleck phase, where (see Eq. (12)) $h_s = \sqrt{D^2 - 2D(I + |J|)}$, the nonmagnetic, $s = 0$, state is stable, and to the region $h_s \leq h_{\parallel} \leq h_{flip}$ of the antiferromagnetic phase (up till the point h_{flip} of its flipping). It is obviously, that at the point (see Eq. (10)) $h_{\parallel} = h_{flip}$, which is corresponded to the value $\theta = 0$, the polarization arrives to its maximum value $s = 1$ on the site.

Using Eq. (17), the behavior $s(h_{\parallel})$ in the fields $h_s \leq h_{\parallel} \leq h_{flip}$ can be found, and from Eq. (10) – also angle θ . After that, it is not difficult to define the field dependence of the

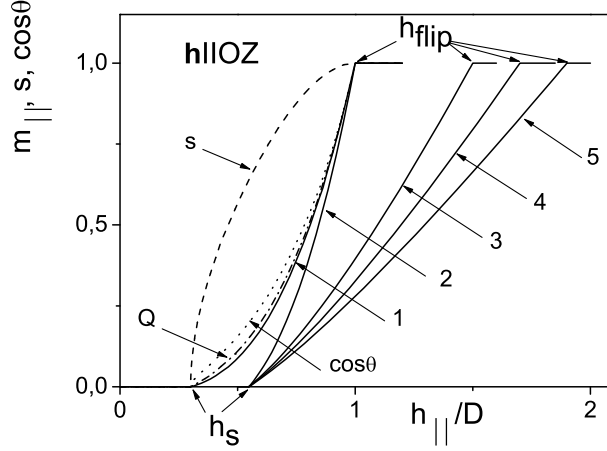


Рис. 1: Magnetization m_{\parallel} (solid curves), spin s , quadrupole moment Q and value of $\cos\theta$ versus field. The curves for s , Q and $\cos\theta$ are calculated at $|J|/D = 0.455$ and at condition $I = J_Z = 0$. Magnetization lines 1-5 are for next parameters: line 1 is for $|J|/D = 0.455$, $I = J_Z = 0$; line 2 is for $|J|/D = 0.35$, $I = J_Z = 0$; line 3 is for $|J|/D = 0.35$, $I = 0$, $J_Z/D = 0.5$; line 4 is for $|J|/D = 0$, $I/D = 0.35$, $J_Z = 0$; line 5 is for $|J|/D = 0.15$, $I/D = 0.2$, $J_Z/D = 0.5$.

quadrupole Q_{α}^{ZZ} in Eq. (3). In the framework of such an approach the field dependencies of magnetization were calculated (see Fig.1).

The curve 1 on Fig.1 was plotted for such case, when intrasublattice exchange is prevailing, while intersublattice and anisotropic ones are omitted. At chosen parameters the magnetic sublattices are fixed artificially, because this extreme case corresponds actually to the two independent antiferromagnets. The field dependencies for s , $Q_{\alpha}^{ZZ} \equiv Q$ and $\cos\theta$ are also shown on Fig.1 for these parameters. It can be seen, that at the point $h_{\parallel} = h_s$ the average site spin really spontaneously appears, and exists in the region $h_{\parallel} > h_s$. With further field growth, the value of s is increasing, leading by velocity of the change of angle θ . This velocity, however, becomes more fast, when the field approaches to the flipping field and, correspondingly, $s \rightarrow 1$. In such a case the intrasublattice exchange (due to its isotropy) has no effect on spin saturation, and so the value h_{flip} of this critical field is completely defined by the single-ion anisotropy.

From curve 1, that refers to the case $D - 2|J| \ll D$, it follows, that the fields h_{flip} and h_s differ quite weakly ($h_{flip}/h_s \approx 3$), although in the experiment [22,23] their ratio

reaches 6, and from the data of Ref. [30] this ratio is about 8. Besides, the field dependence of magnetization for the considered case $I = 0$ reveals, as can be seen, large nonlinearity, while the experimental data for all above mentioned compounds, are evidence of near linear dependence of magnetization on magnetizing force.

It should be noted, that the case, in which inequality $(D - 2|J|)/D \ll 1$ is satisfied, is physically available, but it can not be justified from the experimental point of view. To demonstrate this on Fig. 1 the curve 2 is plotted, for which the difference between parameters in intrasublattice exchange and single-ion anisotropy is chosen not less, but bigger than for curve 1. This choice really leads to the increase of the field value h_s and do the decrease of the ratio h_{flip}/h_s , what indicates, that in attempts of interpretation of the experimental magnetization, the intersublattice exchange can not be neglected.

It is interesting, that when $I/D \rightarrow 0$, Eq. (17) has an exact solution, using which the ground state energy can be written in the form of function of magnetic field:

$$E_{gr} = \frac{1}{4D^2|J|} \left(h_{\parallel}^2 - h_s^2 \right)^2. \quad (18)$$

Then the magnetization (normalizing on one magnetic ion again) takes next form:

$$m_{\parallel} = -\frac{\partial E_{gr}}{\partial h_{\parallel}} = \frac{h_{\parallel}}{2D^2|J|} \left(h_{\parallel}^2 - h_s^2 \right). \quad (19)$$

The dependence (19) is described by the lines 1 and 2 on Fig. 1. From Eqs. (18) and (19) it can be also seen quite a big field nonlinearity of magnetization in the antiferromagnetic phase. The expression (19), for fields $h_{\parallel} \rightarrow h_s$ can be also presented in the form of Eq. (16), when $2|J| \rightarrow D$.

Now let consider the opposite limiting case, when intersublattice exchange is the biggest one in the system. It is seen, that even if one preserves the exchange field (which formally gives the same value of h_s), which affects on the spin from other sublattice, the change of magnetization (curve 4 on Fig. 1) occurs. The antiferromagnetic (intersublattice) exchange, unlike the intrasublattice one, leads to the growth of the field h_{flip} , because in this case the external field should overcome the effect of the same anisotropy, from one side, and, from the other side, – of exchange field, that prevents parallel orientation of sublattice spins.

The curve 3 already shows the nonlinearity decrease in $m(h_{\parallel})$, which as if it is rectified by intersublattice exchange (or by its anisotropic part). At the same time, the antiferromagnetic exchange together with the external magnetic field (in the region $h_{\parallel} > h_s$), resisting the anisotropy, leads to the establishment of spontaneous polarization. In the large fields, when

polarization tends to its maximum value, the behavior of exchange in Van Vleck antiferromagnet does not differ from that one in classical antiferromagnets: it simply resists to the parallel configuration of both sublattice spins.

Curves 3 and 5 demonstrate the influence of easy-plane exchange anisotropy. Actually this anisotropy does not change the position of critical field h_s , but it also does not "want" the establishment of collinear state, when $\mathbf{s}_1 \rightarrow \mathbf{s}_2 \parallel OZ$. At the same time the account of exchange anisotropy of easy-plane type allows to obtain such a behavior of magnetization, that is near to linear one and observed in Refs. [22,23,29,30]. For clarifying how good the linear dependence corresponds to $m(h_{\parallel})$, there is shown on Fig. 2 the magnetic susceptibility $\chi_{\parallel} = dm_{\parallel}/dh$ for the same parameters as on the Fig. 1.

Because the magnetization is nothing other, then $m_{\parallel} = s \cos \theta$, where $s = s(h_{\parallel})$, the longitudinal magnetic susceptibility of Van Vleck magnets is naturally to represent in the form of two above mentioned terms – the classical χ_{cl} and the quantum χ_{quan} ones, so that

$$\chi_{\parallel} = \chi_{cl} + \chi_{quan};$$

$$\chi_{cl} = s \sin \theta \frac{\partial \theta}{\partial h}; \quad \chi_{quan} = \cos \theta \frac{\partial s}{\partial h}. \quad (20)$$

As can be seen from Fig. 1, near h_s the biggest growth reveals the spin polarization s , so in the fields $h_{\parallel} \rightarrow h_s$ the "quantum" contribution will dominate in the magnetic susceptibility. And when the value of spin polarization saturates ($s(h_{\parallel} \rightarrow h_{flip}) \rightarrow 1$), the susceptibility will be mainly controlled by classical term (see Eq. (20)).

Figure 2 shows, that when intrasublattice exchange is really largest one, then magnetic susceptibility grows, changing in field region $h_s \leq h_{\parallel} \leq h_{flip}$ in four times. If intersublattice exchange and/or exchange anisotropy "switches" on, then field dependence of differential magnetic susceptibility $\chi_{\parallel} \equiv \chi(h_{\parallel})$ becomes essentially weaker. Nevertheless, it can be seen from plots, shown on Fig. 1, that nonlinearity of function $m(h_{\parallel})$ in the antiferromagnetic phase at the chosen parameters remains quite noticeable.

The case, when within the boundaries of this phase the value of $\chi(h_{\parallel})$ changes (30-50%), is shown on Fig. 3, which meets the model parameters $|J|/D = 0.05$, $I/D = 0.3$, $J_Z/D = 1$ or $J_Z/D = 1.5$. In other words, the exchange anisotropy is comparable or even exceeds the single-ion one. At such ratios between the parameters the field h_{flip} is almost in five times exceeds the field h_s (one should note, that experimentally observed ratio is $h_{flip}/h_s \approx 6$ [22,23]).

On the same Fig. 3 the dependencies of $s(h_{\parallel})$, $\cos \theta(h_{\parallel})$ and $Q(h_{\parallel})$ are shown for parameters $|J|/D = 0.05$, $I/D = 0.3$ and $J_Z/D = 1$. The behavior of $Q(h_{\parallel})$ almost coincides

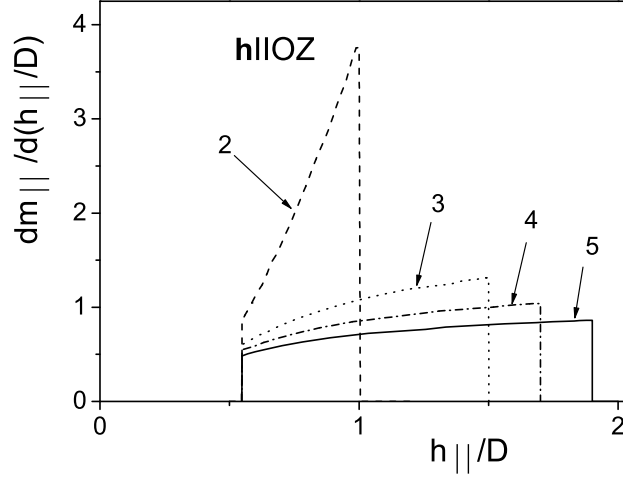


FIG. 2: Magnetic susceptibility $\chi_{||}$ versus field. The numbers of curves are corresponded with parameters, that were used for the plotting of lines with the same numbers, that are on Fig. 1

(see Fig. 1) with the field dependence $m(h_{||})$. Moreover, it follows from Fig. 3, that exchange anisotropy, even a comparable with single-ion one, do not fully linearize the function $m(h_{||})$. As was mentioned, this fact can be explained by the existence of two different regions in the magnetization of Van Vleck magnet.

On the first of these regions, near h_s , the quantum process, as was pointed out, is determinant and the magnetization is defined basically by the appearance and growth of $s(h_{||})$. On the second one, in the vicinity of $h_{||} \leq h_{flip}$, the more important becomes the classical rotation of sublattice spins to the field direction, at essentially less (but not absent) role the very spin value change. It is obvious, that in this region the susceptibility depends much weaker on the value of magnetic field. So, it can be supposed, that the flipping of tilted antiferromagnetic sublattices, or the transition of Van Vleck system between induced two- and one-sublattice magnetically ordered states occurs as an orientation phase transition in ordinary antiferromagnet, when the variation of sublattice magnetization directions is in fact the only process.

However, even for this field transition the quasiclassical approach do not give the correct solution for $m(h_{||})$ in spin nematic. Indeed, one could suppose, that near the flipping field, when $s(h_{||} \rightarrow h_{flip}) \approx 1$, the quasiclassical magnetic energy in the ground state takes the

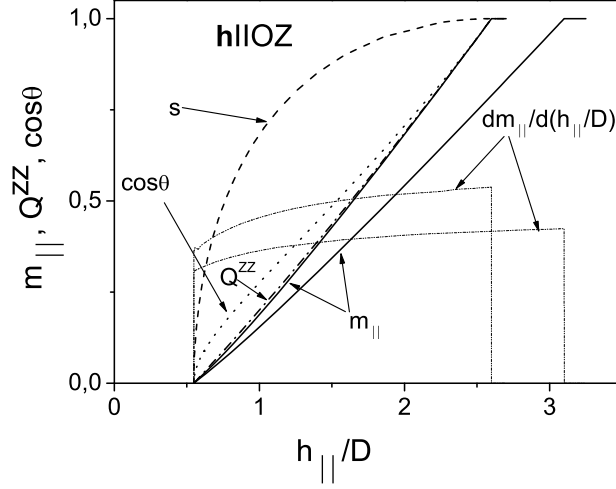


Рис. 3: Longitudinal magnetization m_{\parallel} and magnetic susceptibility χ_{\parallel} versus field at $|J|/D = 0.05$, $I/D = 0.3$, $J_Z/D = 1$ and 1.5 . The functions $s(h_{\parallel})$, $\cos\theta(h_{\parallel})$ and $Q(h_{\parallel})$ are shown only for $|J|/D = 0.05$, $I/D = 0.3$, $J_Z/D = 1$.

form:

$$E_{gr} = I \cos 2\theta + (J_Z + D) \cos^2 \theta - 2h_{\parallel} \cos \theta = 0. \quad (21)$$

Then from Eq. (21) immediately follows the equation

$$\frac{dE_{gr}}{dh_{\parallel}} = 2 [-(2I + J_Z + D) \cos \theta + h_{\parallel}] \sin \theta = 0, \quad (22)$$

which shows, that in the vicinity of $h_{\parallel} \rightarrow h_{flip}$ the magnetization of tilted ($\theta \neq 0$) phase is proportional to the field: $m_{\parallel} = \tilde{\chi}_{\parallel} h_{\parallel}$, where

$$\tilde{\chi}_{\parallel} = \frac{1}{D + 2I + J_Z} \equiv \frac{1}{h_{flip}} = const. \quad (23)$$

It can be seen, that in the field h_{flip} , the magnetization (on one spin) is $m_{\parallel} = 1$. However, the susceptibility (23) differs from the exact ratio (20) and gives physically incorrect behavior of magnetization. It is connected with the fact, that in the region $h_{\parallel} \rightarrow h_{flip}$ it appears, that m_{\parallel} depends linearly versus magnetic field, and asymptotically tends to zero at $h_{\parallel} \rightarrow 0$. As for plots, shown on Figs. 1 and 3, it is easy to see, that the function $m(h_{\parallel})$, although it behaves linearly by field, but nevertheless it depends on magnetic field in not a direct proportion.

An important conclusion follows from this: the quasiclassical approach (21), based on the substitution of quadrupole moment Q^{ZZ} by the average spin Zth projection square, appears to be unapplicable even in such a field region, where spin polarization almost reaches its saturation value $s \rightarrow 1$.

5 Field behavior of magnetization in transversal field

As it was reminded, the phase transition to the antiferromagnetic state does not occur at $\mathbf{h} \perp OZ$, although the magnetic field magnetizes the system.

Lets suppose, that due to the antiferromagnetic exchange in the easy plane, two sublattices are formed. Then their spins lay in this plane and are identically tilted to the field. In this case the energy of the ground state is:

$$E_{gr} = I \cos 2\varphi \cos^2 2\phi - |J| \cos^2 2\phi + D(1 + \sin 2\phi) - 2h_{\perp} \cos \varphi \cos 2\phi, \quad (24)$$

where φ is the angle between vector \mathbf{s}_1 (or vector \mathbf{s}_2) and field \mathbf{h} , and the angle between \mathbf{s}_1 and \mathbf{s}_2 is twice larger, 2φ .

The spin configuration will be defined, as always, by minimizing the energy (24). As a result, it is the set of equations (cp. Eqs. (7) and (8)):

$$\frac{\partial E_{gr}}{\partial \varphi} = -2I \cos^2 2\phi \sin 2\varphi + 2h_{\perp} \sin \varphi \cos 2\phi. \quad (25)$$

$$\frac{\partial E_{gr}}{\partial \phi} = -2(I \cos 2\phi - |J|) \sin 4\phi + 2D \cos 2\phi + 4h_{\perp} \cos \varphi \sin 2\phi = 0 \quad (26)$$

The equation (25) has two solutions. For the first of them $\varphi = 0$ and it corresponds to one-sublattice magnetization, when the polarization of magnetic ions is directed along the field. The second solution $\cos \varphi = h_{\perp}/(2I \cos 2\phi)$ provides the existence of two sublattices. The last, taking into account Eq. (5), can be rewritten in the usual form:

$$\cos \varphi = h_{\perp}/2Is. \quad (27)$$

The denominator of Eq. (27) is the intersublattice exchange field, and this expression is similar to the expression for the magnetic sublattice tilt angle in classical antiferromagnets [1,2]. Nevertheless, it should be noted, that spin in Eq. (27) is not equal to its maximum value.

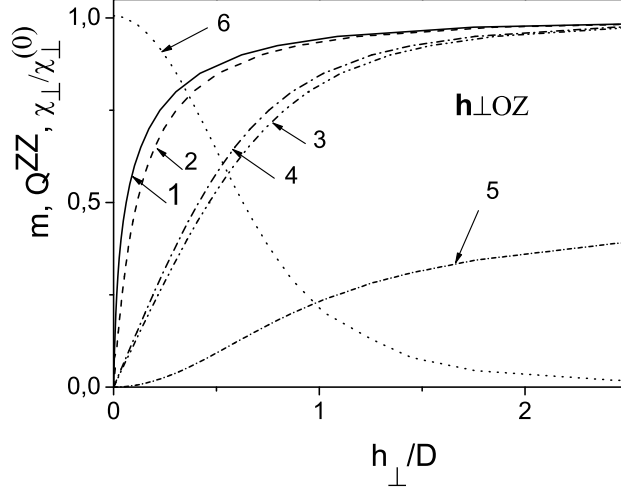


Рис. 4: Field behavior of $m(h_{\perp})$ (lines 1-4), $Q^{ZZ}(h_{\perp})$ (line 5) and χ_{\perp} for $\mathbf{h} \perp OZ$. The line 1 is calculated for parameters $|J|/D = 0.455$, $I = 0$, the line 2 is for $|J|/D = 0.35$, $I = 0$, the line 3 is for $|J|/D = 0$, $I = 0.35$, lines 4-6 are for $|J|/D = 0.05$, $I = 0.3$

Substituting (27) in (26), one arrives to the equation:

$$2[2(I + |J|)\sin 2\phi + D]\cos 2\phi = 0 \quad (28)$$

It follows from Eq. (28), that the spin polarization for antiferromagnetic state at $\mathbf{h} \perp OZ$ should be equal to (9). However, the model parameters, accepted above, are such, that the denominator under the root in Eq. (9) is larger than 1, and non-polarized singlet is the ground state of ions. Thus, the solution (27) is possible only for initially polarized ground state, or when the antiferromagnetic (not singlet) phase is realized in the system even at $h_{\perp} = 0$. But if without field the polarization is $s = 0$, then from the set of Eqs. (25)-(26) fundamentally another result follows: the critical field of polarization appearance in the transversal geometry is the $h_{\perp} = 0$. The distinction from "longitudinal" case, for which the critical field is finite, is easy to explain. At any fields $h_{\perp} \neq 0$ the ground state with $S_Z = 0$ (in crystal coordinate system) is immediately admixed with the ionic excited states, which have $S_Z = \pm 1$. In the case of longitudinal field, there is a threshold for such an admixture. Then taking into account, that the transversal field does not induce the antiferromagnetic phase, one can obtain:

$$E_{gr} = (I - |J|) s^2 + D \left(1 - \sqrt{1 - s^2} \right) - 2h_{\perp} s. \quad (29)$$

It should be also noted, that at $\mathbf{h} \perp OZ$ the spin polarization is always equal to magnetization, which is directed along \mathbf{h} , i.e. $m_{\perp} = s$. Minimizing energy (29), one readily arrives to the equation

$$\frac{\partial E_{gr}}{\partial s} = 2(I - |J|)s + D \frac{s}{\sqrt{1 - s^2}} - 2h_{\perp} = 0, \quad (30)$$

that allows to define the dependence of spin polarization upon the transversal field.

On Fig. 4 there is shown the field behavior for m_{\perp} , that are obtained from Eq. (30). It is seen, that if intrasublattice exchange dominates in the system, then the magnetization increases rapidly, and if intersublattice exchange is "added" then the magnetization slows down.

Despite the fact, that at $\mathbf{h} \perp OZ$ the average spins are oriented also perpendicularly to Z , the spin quadrupole moment Q^{ZZ} versus field reveals the behavior (see Fig.4) similar to the spin polarization. The magnetization rate decreases as the field grows and the magnetic susceptibility has a maximum at $h_{\perp} \rightarrow 0$. The normalized magnetic susceptibility $\chi_{\perp}^{(0)} = \chi(h_{\perp} = 0)$ is also plotted on Fig. 4.

Using Eq. (30), the expression for magnetic susceptibility at $\mathbf{h} \perp OZ$ can be obtained; it has the form:

$$\chi_{\perp} \equiv \chi(h_{\perp}) = \frac{1}{2(I - |J|) + D(1 - s^2)^{-3/2}} \quad (31)$$

It is seen, that in large fields, when $s \rightarrow 1$, transversal susceptibility $\chi_{\perp} \rightarrow 0$. In the opposite limit $h_{\perp} \rightarrow 0$, the magnetic susceptibility is equal to:

$$\chi_{\perp}^{(0)} = \frac{2}{D + 2(I - |J|)} \quad (32)$$

It also follows from Eq. (32), that when the intrasublattice exchange increases the value of $\chi_{\perp}^{(0)}$ grows and, on the contrary, at the increasing of intersublattice exchange it decreases. It is usual situation for physics of phase transitions, because the growth of intrasublattice exchange at $I = 0$ can result in ferromagnetic state with characteristic to such kind of transition the susceptibility singularity (it goes to the infinity at the transition point). At the same time, the transition to the antiferromagnetic state is not accompanied by the abnormal growth of magnetic susceptibility. Indeed, the point of phase transition to the

antiferromagnetic phase corresponds the equality $D = 2(I + |J|)$. At its substitution in Eq. (32) the value $\chi_{\perp}^{(0)} = 1/2I$ is directly obtained. The same will be the value of magnetic susceptibility in the antiferromagnetic phase, the magnetization of which is determined by the expression (27).

6 Induced magnetostriction in the longitudinal magnetic field

Considering the striction properties of Van Vleck antiferromagnets, it will be for certainty supposed, that the crystal has a hexagonal structure. There will be confined, at that, in magneto-elastic energy (see Eq. (1)) by spin-deformation interaction, that is proportional to second power of average spin [45]. Besides the single-ion terms will be accounted in the energy E_{m-el} ; they contain the average components of spin quadrupole moment [46,47]. Then for such approaches the elastic and magneto-elastic contributions to the total energy (1) can be presented as following:

$$E_{el} = \frac{1}{2}c_{11}(u_{xx}^2 + u_{yy}^2) + \frac{1}{2}c_{33}u_{zz}^2 + c_{12}u_{xx}u_{yy} + c_{13}(u_{xx} + u_{yy})u_{zz} + 2c_{44}(u_{xz}^2 + u_{yz}^2) + 2c_{66}u_{xy}^2 \quad (33)$$

$$\begin{aligned} E_{m-el} = & \sum_{\alpha\beta} [\lambda_{\alpha\beta}u_{zz} + \gamma_{\alpha\beta}(u_{xx} + u_{yy})] \mathbf{s}_{\alpha}\mathbf{s}_{\beta} + \sum_{\alpha} \left[B_{11}^{(s-i)} (Q_{\alpha}^{XX}u_{xx} + Q_{\alpha}^{YY}u_{yy}) \right. \\ & + B_{33}^{(s-i)} Q_{\alpha}^{ZZ}u_{zz} + B_{12}^{(s-i)} (Q_{\alpha}^{XX}u_{yy} + Q_{\alpha}^{YY}u_{xx}) + 4B_{44}^{(s-i)} (Q_{\alpha}^{YZ}u_{yz} + Q_{\alpha}^{XZ}u_{xz}) \\ & \left. + 4B_{66}^{(s-i)} Q_{\alpha}^{XY}u_{xy} \right] + \sum_{\alpha\beta} \left\{ B_{11}^{(\alpha\beta)} (s_{\alpha}^X s_{\beta}^X u_{xx} + s_{\alpha}^Y s_{\beta}^Y u_{yy}) + B_{33}^{(2)} s_{\alpha}^Z s_{\beta}^Z u_{zz} \right. \\ & \left. + B_{12}^{(\alpha\beta)} (s_{\alpha}^X s_{\beta}^X u_{yy} + s_{\alpha}^Y s_{\beta}^Y u_{xx}) + 4B_{44}^{(\alpha\beta)} (s_{\alpha}^Y s_{\beta}^Z u_{yz} + s_{\alpha}^X s_{\beta}^Z u_{xz}) + 4B_{66}^{(\alpha\beta)} s_{\alpha}^X s_{\beta}^Y u_{xy} \right\}, \end{aligned} \quad (34)$$

where $\lambda_{\alpha\beta}$, $\gamma_{\alpha\beta}$ are the parameters of magneto-elastic exchange interactions, in which indices α , β , as above, are the numbers of the spin sublattices, $B_{jl}^{(s-i)}$ and $B_{jl}^{(\alpha\beta)}$ are the parameters of anisotropic magneto-elastic interactions [45], where the upper index shows on the single-ion or ionic origin, correspondingly; u_{ij} are the components of elastic deformation tensor, c_{jl} are the coefficients of elasticity. It should be noted, that single-ion magneto-elastic interactions in Eq. (34) are written in the crystallographic coordinate systems XYZ, so, as distinct from Eq. (5), the indices of quadrupole moment components $Q^{jl} = \frac{1}{2}\langle s^j s^l + s^k s^l \rangle$ are also defined in this system.

The values of elastic deformations, which appear because of spin configuration change, will be found by the minimization of energies (33) and (34) by corresponding components of deformation tensor. As a result the following expressions are obtained:

$$u_{xx} + u_{yy} = -\frac{1}{c_{11} + c_{12} - 2c_{13}^2/c_{33}} \left[2 \sum_{\alpha\beta} \gamma_{\alpha\beta} \mathbf{s}_\alpha \mathbf{s}_\beta + \sum_{\alpha} \left(B_{11}^{(s-i)} + B_{12}^{(s-i)} \right) (Q_\alpha^{XX} + Q_\alpha^{YY}) \right. \\ \left. + \sum_{\alpha\beta} \left(B_{11}^{(\alpha\beta)} + B_{12}^{(\alpha\beta)} \right) (s_\alpha^X s_\beta^X + s_\alpha^Y s_\beta^Y) - \frac{2c_{13}}{c_{33}} \left(\sum_{\alpha\beta} \lambda_{\alpha\beta} \mathbf{s}_\alpha \mathbf{s}_\beta + \sum_{\alpha} B_{33}^{(s-i)} Q_\alpha^{ZZ} \right) \right. \\ \left. + \sum_{\alpha\beta} B_{33}^{(\alpha\beta)} s_\alpha^Z s_\beta^Z \right], \quad (35)$$

$$u_{xx} - u_{yy} = -\frac{1}{c_{11} - c_{12}} \left[\sum_{\alpha} \left(B_{11}^{(s-i)} - B_{12}^{(s-i)} \right) (Q_\alpha^{XX} - Q_\alpha^{YY}) + \sum_{\alpha\beta} \left(B_{11}^{(\alpha\beta)} - B_{12}^{(\alpha\beta)} \right) \times \right. \\ \left. \times (s_\alpha^X s_\beta^X - s_\alpha^Y s_\beta^Y) \right], \quad (36)$$

$$u_{zz} = -\frac{(c_{11} + c_{12})}{c_{33}(c_{11} + c_{12}) - 2c_{13}^2} \left[\sum_{\alpha\beta} \lambda_{\alpha\beta} \mathbf{s}_\alpha \mathbf{s}_\beta + \sum_{\alpha} B_{33}^{(s-i)} Q_\alpha^{ZZ} + \sum_{\alpha\beta} B_{33}^{(\alpha\beta)} s_\alpha^Z s_\beta^Z \right. \\ \left. - \frac{c_{13}}{c_{11} + c_{12}} \left\{ 2 \sum_{\alpha\beta} \gamma_{\alpha\beta} \mathbf{s}_\alpha \mathbf{s}_\beta + \sum_{\alpha} \left(B_{11}^{(s-i)} + B_{12}^{(s-i)} \right) (Q_\alpha^{XX} + Q_\alpha^{YY}) \right. \right. \\ \left. \left. + \sum_{\alpha\beta} \left(B_{11}^{(\alpha\beta)} + B_{12}^{(\alpha\beta)} \right) (s_\alpha^X s_\beta^X + s_\alpha^Y s_\beta^Y) \right\} \right]. \quad (37)$$

The Eq. (35) determines the isotropic striction of "easy" plane, or, what is the same, its expansion (or its contraction, depending on the signs of magneto-elastic coefficients), and Eq. (37) – the expansion/contraction along the crystal symmetry axis.

The spontaneous deformation in singlet phase is defined by obtained Eqs. (35)-(37) after substitution in them corresponding values of spin variables: $s = 0$, $Q^{ZZ} = 0$, $Q^{XX} = Q^{YY} = 1$. After this it follows, that in this phase only the isotropic deformation of "easy" plane and expansion/constriction will be not equal to zero:

$$u_{xx}^{(0)} + u_{yy}^{(0)} = -4 \frac{B_{11}^{(s-i)} + B_{12}^{(s-i)}}{c_{11} + c_{12} - 2c_{13}^2/c_{33}}, \quad (38)$$

$$u_{zz}^{(0)} = 4 \frac{c_{13} (B_{11}^{(s-i)} + B_{12}^{(s-i)})}{(c_{11} + c_{12}) c_{33} - 2c_{13}^2}, \quad (39)$$

where index (0) refers to the spontaneous magnetostriction. It can be seen, that in singlet phase the spontaneous deformations are defined only by single-ion magneto-elastic coefficients and satisfy the ratios: $u_{xx}^{(0)} = u_{yy}^{(0)} = -u_{zz}^{(0)} c_{33}/2c_{13}$. The expressions (38) and (39) remain

correct in the magnetic field too, while $h_{\parallel} < h_s$, i.e. in the region of the singlet phase stability. In other words, the striction, that is specified in this region by Eqs. (38)-(39), does not depend on the field.

The induced striction appears only after the spin polarization occurrence, or in the fields $h_{\parallel} > h_s$ [47], and is described by Eqs. (35)-(37). They were written in the general form and included all admitted phenomenological parameters of magneto-elastic coupling, that has both exchange (inter-ionic) and single-ion (because of the change of crystal field, that affects the ions) origin. So, at the analysis of magnetostriction, it should be considered several, by our opinion, interesting cases.

At first, let consider the magnetostiction, that is caused by isotopic exchange interaction. In the most of magnets, the corresponding magneto-elastic coupling does not depend on spin directions and usually exceeds the anisotropic magneto-elastic one on more then order of magnitude. However, it is easy to convince, that despite the fact, that exchange magneto-elastic interaction does not depend on spin directions in crystal, the striction, that is generated by the external field, can be anisotropic.

Indeed, it will be supposed, that in Eq. (34) only the magneto-elastic coefficients are finite $\lambda_{12} \neq 0$, $\gamma_{11} \neq 0$, and also $c_{13} \rightarrow 0$. Such a situation can take place, for example, in the lamellar crystals. If magnetic sublattices are formed by spins in basal planes, then the intersublattice antiferromagnetic exchange depends basically on inter-atomic distances along the crystal symmetry axis. As for intrasublattice one, it depends on the inter-ionic distances in this plane. Then from Eqs. (38) and (39) one can find, that in singlet phase all $u_{jj}^{(0)} = 0$ and it is not influenced by the field. When spin polarization becomes finite, the exchange magnetostriction is represented by quite simple ratios:

$$\frac{u_{xx}}{u_{xx}^{flip}} = \frac{u_{yy}}{u_{yy}^{flip}} = s^2 = s^2 \quad (40)$$

$$\frac{u_{zz}}{u_{zz}^{flip}} = s_1 s_2 = s^2 \cos 2\theta \quad (41)$$

where 2θ is, as above, the angle between sublattice spins, $u_{xx}^{flip} = u_{yy}^{flip} = -2\gamma_{11}/(c_{11} + c_{12})$ and $u_{zz}^{flip} = -2\lambda_{12}/c_{33}$ are the values of induced striction at $h_{\parallel} = h_{flip}$. It should be noted, that for this case $u_{xx}^{(0)} = u_{yy}^{(0)} = u_{zz}^{(0)} = 0$ also.

It follows from Eqs. (40) and (41), that in the region near $h_{\parallel} \rightarrow h_s$ of induced by external field phase transition there are singularities in striction field dependencies. The derivatives $\partial u_{zz}/\partial h_{\parallel}$ and $\partial u_{xx}/\partial h_{\parallel}$ will have a jump at this point.

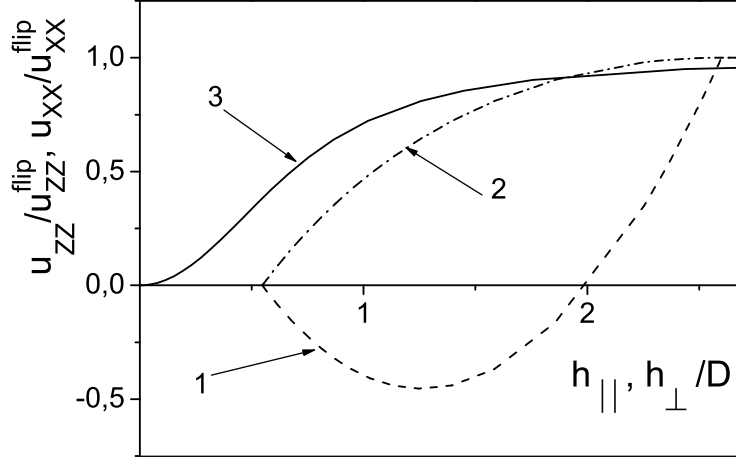


Рис. 5: Exchange striction, which is described by Eqs. (40) and (41), for parameters $|J|/D = 0.05$, $I/D = 0.3$, $J_Z/D = 1$. The line 1 corresponds to the "longitudinal" deformation, u_{zz}/u_{zz}^{flip} , and line 2 – to the "transversal" one u_{xx}/u_{xx}^{flip} at $\mathbf{h} \parallel OZ$. The line 3 corresponds to the "longitudinal" deformation at $\mathbf{h} \perp OZ$.

The field behavior of induced exchange striction, that is defined by Eqs. (40) and (41), is shown on Fig. 5. It can be seen, that in the field $\mathbf{h} \parallel OZ$ the exchange striction (it is normalized and – depending on the sign of γ_{11} – can be both positive or negative), that is caused by the intrasublattice interaction, does not change its sign and only "follows" the behavior $s^2(h_{\parallel})$. At the same time, the striction, that is originated from intersublattice exchange (its sign depends on the sign of λ_{12}) for such a field orientation, is non-monotonic. This fact is a direct and simple consequence of change of $\cos 2\theta$ sign. At first, the spin polarization grows (during the increasing of the field above h_s) practically at the opposite spin directions, so the striction (by absolute value) also increases. However, the further field growth gives rise to spin sublattice tilt, which becomes more and more noticeable, and in its own turn it causes the decreasing and passing through zero at $\theta = \pi/4$ of deformation. After such an angle configuration, when $\theta \rightarrow 0$, the magnetostriction again increases, reaching the maximum in the field $h_{\parallel} = h_{flip}$.

According to Eqs. (40) and (41) the field behavior of u_{xx} and u_{zz} at $\mathbf{h} \perp OZ$ will be similar. The exchange induced striction in this field changes monotonously, but begins to appear at the point $h_{\perp} = 0$. It should be noted, that in the region $h_{\perp} \rightarrow 0$ the striction is proportional to the h_{\perp}^2 . Here also the derivatives $\partial u_{zz}/\partial h_{\perp}$ and $\partial u_{xx}/\partial h_{\perp}$ changes continuously without jumps.

Thus, the main distinction of induced striction at $\mathbf{h} \parallel OZ$ and $\mathbf{h} \perp OZ$ is, that in the

longitudinal field there should be a jump in the field derivative of striction behavior versus field, and in the transversal field this derivative changes continuously.

Let note, that field behavior of magnetostriction, shown on Fig. 5, is qualitatively agreed with experimental data, which are obtained from the measurement of DTN deformation [22,23]. Indeed, in this compound the intersublattice exchange dominates and resulting from it the magneto-elastic coupling refers to chains Ni-Cl-Ni-Cl, which are parallel to the axis OZ . It is still unknown, whether Ni ions, which lie in the one basal plane, form the one sublattice, because the nearest chains are shifted on the half of a period along axis OZ . But, nevertheless, there are no doubts, that in this singlet magnet the determinant (together with single-ion anisotropy) is the intersublattice (antiferromagnetic) exchange and its anisotropy.

It is also not excluded, that in singlet magnets the anisotropy of magneto-elastic interaction can be comparable with isotropic one. The anisotropic part of magneto-elastic coupling may include both exchange (interion) and single-ion parts [4]. Furthermore, it should be so in fact, if the magnetic system, to which DTN refers, is associated with strong single-ion anisotropy (which is the evidence of the essential spin-orbital interaction. In DTN, that is described by Hamiltonian (2), the single-ion anisotropy essentially exceeds the exchange interaction, the consequence of what is the formation of singlet ground state of the magnet in whole. So, in this case it is possible the next situation: the striction, that is caused by anisotropic interactions, exceeds the one, which is originated from isotropic exchange.

As one more example, let consider such a case, when all magneto-elastic coefficients, except for $B_{33}^{(s-i)}$ and $B_{33}^{(\alpha\beta)}$, can be neglected. Then, if also $c_{13} \rightarrow 0$, the main will be, as it is seen from Eq. (27), the deformation of crystal along axis OZ :

$$u_{zz} = -\frac{2}{c_{33}} \left[B_{33}^{(s-i)} Q_{\alpha}^{ZZ} + \left(B_{33}^{(11)} + B_{33}^{(12)} \right) (s \cos \theta)^2 \right]. \quad (42)$$

This expression for striction can be written in the normalized form:

$$\frac{u_{zz}}{u_{zz}^{flip}} = \frac{B_{33}^{(s-i)} Q_{\alpha}^{ZZ} + \left(B_{33}^{(11)} + B_{33}^{(12)} \right) (s \cos \theta)^2}{B_{33}^{(s-i)} + B_{33}^{(11)} + B_{33}^{(12)}}, \quad (43)$$

where according to the definition

$$u_{zz}^{flip} = -\frac{2}{c_{33}} \left(B_{33}^{(s-i)} + B_{33}^{(11)} + B_{33}^{(12)} \right)$$

is the striction in the field $h_{\parallel} = h_{flip}$.

It is shown on Fig. 6 the field behavior of induced striction, which is obtained, using Eq. (43). The most interesting case is $\mathbf{h} \parallel OZ$, when $B_{33}^{(s-i)} \neq 0$, and $B_{33}^{(11)} + B_{33}^{(12)} =$

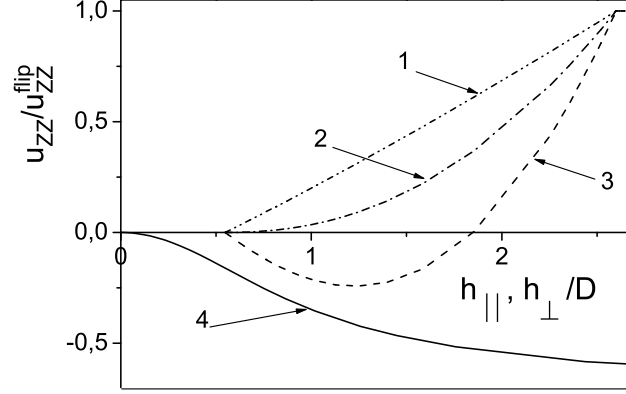


Рис. 6: "Longitudinal" u_{zz}/u_{zz}^{flip} magnetostriction *versus* field. Line 1 is satisfied at $B_{33}^{(s-i)} \neq 0$ and $B_{33}^{(11)} + B_{33}^{(12)} = 0$, the line 2 - $B_{33}^{(s-i)} = 0$, $B_{33}^{(11)} + B_{33}^{(12)} \neq 0$, the line 3 - $(B_{33}^{(11)} + B_{33}^{(12)}) / (B_{33}^{(s-i)} + B_{33}^{(11)} + B_{33}^{(12)}) = 2.5$, $B_{33}^{(s-i)} / (B_{33}^{(s-i)} + B_{33}^{(11)} + B_{33}^{(12)}) = -1.5$ for $\mathbf{h} \parallel OZ$. The line 4 is obtained for the same parameter values as for line 3, but at $\mathbf{h} \perp OZ$

0, to which refers the curve 1 on this figure. Corresponding magnetostriction is in direct proportion to the quadrupole moment Q^{ZZ} . It should be said, that obtained magneto-elastic contribution is linear (but not quadratic, as it is usually) by magnetization, taking into account, that, quadrupole moment as function of field is similar (see Figs. 1 and 3) to the behavior of $m(h_{\parallel})$. It should be also considered, that at the large exchange anisotropy J_Z the magnetization versus $h_{\parallel} - h_s$ changes almost linearly, or $m_{\parallel} \sim h_{\parallel} - h_s$. So one can say, that the magnetostriction too (see line 1 on Fig. 6) behaves almost linearly in a whole region of antiferromagnetic phase existence.

The field behavior of stiction at $\mathbf{h} \parallel OZ$, because of parameters choice, appears to be proportional to the m_{\parallel}^2 , is corresponded with line 2 on Fig. 6.

There is shown also on Fig. 6 the example (line 3) of common action of both anisotropic magneto-elastic striction mechanisms. At these ratios there takes place the competition between single-ion and inter-ion terms. In particular it is seen from line 3 on Fig. 6, that the field behavior of striction, that is caused by the anisotropic magneto-elastic interactions, can be the same as the stiction, that is originated from the isotropic exchange, what is shown on Fig. 5. However, it follows from Eq. (43), that at $\mathbf{h} \parallel OZ$ the single-ion and inter-ion contributions in striction can compete, and at $\mathbf{h} \perp OZ$ there remains only the single-ion one.

The striction behavior in $\mathbf{h} \perp OZ$ is shown as line 4 on Fig. 6, at the same parameters, at which the line 2 was obtained. Thus, in the considered examples of the competition between magneto-elastic interactions, it appeared, that in large fields $\mathbf{h} \parallel OZ$ and $\mathbf{h} \perp OZ$ the longitudinal striction has different signs.

In DTN the components of tensor of longitudinal striction have one sign and are close in the values [22]. Therefore, the assumption, that the induced longitudinal striction at the magnetization in fields $\mathbf{h} \parallel OZ$ and $\mathbf{h} \perp OZ$, that are corresponded to $h_{\parallel,\perp} \rightarrow h_{flip}$ in this compound is caused by the intersublattice isotropic exchange interactions, is quite probable (believable). But, nevertheless, the additional investigations of magneto-elastic properties of the system are needed to prove unambiguously, that the observed deformation, under the effect of the field, is resulted from the interplane (in DTN – intersublattice) exchange interaction only, and is not the consequence of several field contributions, including from the spin quadrupole moment.

7 Conclusions

Thus, it was obtained, that the phase transition to magnetically ordered state, induced by magnetic field, in Van Vleck antiferromagnet, is the quantum phase transition. The spin polarization of the magnetic ion ground state is the order parameter of this phase transition, and for its description the Landau theory can be used. The considered transition is a consequence of competition of different interactions, and, what is important, it appears in the field, that is perpendicular to the easy plane. Such a field does not reduce the symmetry in this plane, leaving all directions in it equivalent. The conservation of degeneracy for sublattice magnetization directions in the easy plane is the crucial symmetrical condition of phase transition to the antiferromagnetic state with spontaneous magnetizations, that are lying in this plane. The account of striction (see Eq. (36)) leads to the spontaneous lowering of the plane symmetry.

It is also shown, that in the magnetic field induced antiferromagnetic phase the spin polarization (magnetization) of sublattice changes continuously from zero, reaching its maximum at the spin flipping point. As distinct from classical Neel antiferromagnets, in the magnetic ordered phase of Van Vleck (singlet) antiferromagnet the magnitude of sublattice magnetization strongly depends on the field. The same dependence on the field has an angle, that defines the deviation of sublattice magnetization from field direction. At the same time, the magnetization of a system as a whole, being weakly dependent from the field, shows almost linear field

behavior (when the exchange anisotropy is also accounted).

The calculations indicate, that in such an antiferromagnet the induced magnetostriction appears only in the magnetic phase. This magnetostriction in the small fields region is connected with the spontaneous formation of sublattice magnetizations. In the large fields (which are corresponded to spin flipping field) the magnetostriction is basically determined by the sublattice magnetization rotation.

Let emphasize two important issues. First one – is the possibility of induced striction, which is originated by the intrasublattice magneto-elastic interaction. In the classical antiferromagnets this part of induced magnetostriction of antiferromagnets is usually neglected, because of the paraprocess smallness. The second aspect – is connected with single-ion striction, the value of which is directly proportional to the spin quadrupole moment; as a result, it occurs that the striction, which is caused by this quantity, has close to linear dependence upon the field.

Finally, the methodic notation should be made. The results, presented above, were obtained using the approximation of self-consistent field. It was supposed, that more accurate calculations will not bring any qualitative results, however they can influence quantitatively. Moreover, the magneto-elastic energy was written in the phenomenological form and contained a lot of parameters. So at the analysis of concrete compounds one should proceed from its characteristic hierarchy of interactions in the magneto-elastic energy, like it was made for example in this article. The separate paper will be devoted to detailed comparison of calculations with the available experimental data.

We are grateful to Prof. S.M. Ryabchenko, who paid our attention on experimental articles [22,23] and the problem of magnetostriction properties of singlet magnets.

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